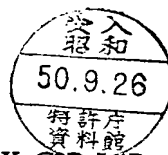


PATENT SPECIFICATION

(11) 1 400 800

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- (21) Application No. 58244/72 (22) Filed 18 Dec. 1972
 (31) Convention Application No. 130 462 (32) Filed 20 Dec. 1971 in
 (33) Canada (CA)
 (44) Complete Specification published 23 July 1975
 (51) INT CL² C08L 71/00/(C08L 71/00, 9/02)
 (52) Index at acceptance
 C3P 2HY
 C3R 27C C12 C13M C22 C28X C6A1 C6X C8P-L4B
 L5X



(54) SULFUR VULCANIZABLE POLYETHER COMPOSITION

(71) We, POLYSAR LIMITED (formerly Polymer Corporation Limited), a company organized under the laws of Canada, of Sarnia, Ontario, Canada, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to halogenated polyether polymers and in particular to sulfur vulcanizable blends of such polymers with nitrile copolymers.

Halogenated polyether polymers such as polyepichlorohydrin or a copolymer of epichlorohydrin and ethylene oxide are essentially saturated polymers and cannot be vulcanized in the presence of sulfur vulcanization agents. Such copolymers can be made sulfur vulcanizable by the introduction of sufficient olefinic unsaturation of at least about 5 mole % e.g. by copolymerizing epichlorohydrin with materials such as allyl glycidyl ether or glycidyl methacrylate.

The object of this invention is to provide an alternative way of making halogenated polyether polymers sulfur vulcanizable. Another object of the invention is to provide sulfur co-vulcanizable compositions of halogenated polyether polymers and olefinically unsaturated elastomers.

According to the present invention there is provided a sulfur vulcanizable elastomeric composition comprising a blend of an epihalohydrin polymer and a crystalline alternating copolymer of (a) a conjugated alkadiene, component (a) containing not less than 40 mole % of a 2-alkyl alkadiene, and (b) an acrylic nitrile, said alternating copolymer being characterized by a crystallinity of 5—35% as measured by X-ray diffraction in its unstretched state, and said composition being substantially free of agents capable of vulcanizing said epihalohydrin polymer.

For the avoidance of doubt, it is pointed out that when referring, herein or in the appended claims, to a given type of monomer,

it is to be understood that that reference includes within its scope a mixture of different specific monomers of that type. Thus, for example, a reference to "an alkadiene" includes within its scope a mixture of alkadienes.

The halogenated polyether polymers which can be used in this invention includes homopolymers of epichlorohydrin or epibromohydrin and their copolymers with each other and/or with up to 50 mole % (preferably 10—50 mole %) of oxirane compounds such as ethylene oxide, propylene oxide, glycidyl compounds. Epihalohydrin copolymers with olefinically unsaturated oxirane compounds may also be used if desired; the unsaturation level of such copolymers need not be high and may range from 0.1 to less than 5 mole %. The preferred halogenated polyether polymers are solid elastomeric materials having a Mooney viscosity (M/L—4' @ 100°C) of about 20 to 150 and a halogen content in the form of halomethyl groups —CH₂X of up to 58% by weight. In the case of epichlorohydrin polymers, the maximum chlorine content is 38.4% and the preferred range is between about 19 and 38% by weight. Such polymers are known in the art and can be prepared by the polymerization of epihalohydrin and, if desired, an oxirane compound in an inert organic solvent in the presence of a catalyst containing a complexed organometallic compound such as aluminum trialkyl-water or alcohol complex, zinc dialkyl-water complex or ferric chloride-glycol complex.

The comonomers are arranged in an alternating manner such that contiguous units of alkadiene or acrylic nitrile are practically eliminated. In the present invention there is employed a novel alternating copolymer characterised in that it is a crystalline alternating copolymer such as is formed by the copolymerization of acrylic nitrile and conjugated alkadiene consisting of 40—100 mole % 2-alkyl alkadiene, such as 2-alkyl butadiene-1,3, preferably isoprene, and 0—60

[Price 33p]

5 mole % other conjugated alkadiene such as butadiene-1,3. These crystalline copolymers showing a crystallinity content of 5—35% as determined by the X-ray diffraction methods and a melting point of 60—100°C are preferably used when a processable elastomeric composition of high green strength is desired.

10 The crystalline alternating polymers used in this invention can be prepared by suitable modification of the copolymerization processes described in U.K. Patent Specifications Nos. 1,186,462 and 1,231,327 using a complex-type catalyst comprising, for example, an organo-aluminum halide complexed with an acrylic nitrile together with a cocatalyst of a transition metal compound. Representative of such a catalyst system is ethyl aluminum dichloride complexed with acrylonitrile with the cocatalyst vanadium oxychloride. In the present preparation, the transition metal compound is used in an amount less than the equimolar amount with respect to the aluminum compound, and the temperature of polymerization is maintained at less than room temperature to favour the formation of a crystalline copolymer. While U.K. Patent Specifications Nos. 1,186,462 and 1,231,327 do not disclose alternating polymers of the type herein defined having crystallinity in their relaxed state at substantially 25°C of 5 to 35%, as measured by X-ray diffraction, it is believed that once having been given the present concept and upon consideration of this disclosure, the artisan familiar with the preparation of crystalline polymers of diolefins would have within his skill the knowledge of suitable conditions whereby to prepare the presently described crystalline alternating polymers.

40 The acrylic nitrile may be acrylonitrile, methacrylonitrile, alkyl substituted acrylonitrile containing 2—6 carbon atoms in the alkyl group, vinylidene cyanide, or methylene glutaronitrile; acrylonitrile, however, is the preferred comonomer.

45 While the bound acrylic nitrile in an alternating copolymer somewhat imperfect as to its alternating structure may vary from a precise 1:1 ratio with the diene monomer unit, the preferred embodiments are those wherein the bound acrylic nitrile content is substantially 50 mole %.

50 The two polymers, the halogenated polyether polymer and the nitrile copolymer, may be blended by any suitable means on conventional rubber mills or in Banbury type internal mixers. They can also be blended in solution and the mixture recovered therefrom. The ratio of the nitrile copolymer to the halogenated polyether polymer in the composition depends on the specific use, but the epichlorohydrin polymer and the copolymer are preferably in a proportion from 90/10 to 10/90 in parts by weight. In applications where a good flexibility at low temperatures and a high resistance to ageing in hot air is required,

the composition preferably contains less than 50 parts by weight, say 10—25 parts by weight, of the nitrile copolymer per 100 parts of polymer mixture. When, on the other hand, the composition is to be used in the production of conveyor belts or vee belts, where a high tensile strength, tear, abrasion resistance and lower specific gravity are desired, the mixture preferably contains from 50—90 parts by weight of the nitrile copolymer per 100 parts of the mixture of polymers.

70 The composition can be compounded with conventional rubber compounding ingredients: carbon black or other reinforcing and non-reinforcing fillers, sulfur, vulcanization accelerator(s), antioxidants and, optionally, extending oils, plasticizers and tackifying resins. The amount of these ingredients may vary within a wide range depending mainly on the properties desired in the final product. For example, carbon black loading may range from 20 to 150 weight parts, per 100 parts of polymeric material.

80 The compounded composition of this invention is substantially free of agents capable of vulcanizing unblended epihalohydrin polymer. Such agents to be avoided include polyamines e.g. ethylene diamine, polyalkylene polyamines, thiourea and substituted thioureas, guanidines, aldehyde amines, 2-mercaptoimidazoline and ammonium salts. Metal oxides and hydroxides of magnesium, bismuth, lead are to be avoided. However, small amounts of about 5 parts or less of zinc oxide per 100 parts by weight of polymeric material may be used, if desired, for more reproducible vulcanization.

105 The composition can be made vulcanizable by including in it, by mixing, sulfur preferably at least 0.5 parts and suitably 0.5 to 3 parts, preferably in the presence of at least 0.5 parts, and suitably 0.5—4 parts, a sulfur vulcanization accelerator, said parts being parts by weight, per 100 parts by weight polymeric material. The accelerator may be selected from dithiocarbamates (e.g. dialkyl dithiocarbamates), thiazoles, thiazyl disulfides (e.g. benzothiazyl disulfide), thiuram sulfides (e.g. tetraalkyl thiuram disulfides) and xanthates; the specific type and the amount of the accelerator and the amount of sulfur is selected so as to give a desired degree of crosslinking when the vulcanization is brought about, by heating, preferably at a temperature ranging from 100°C to 160°C. The absence of polyamines and other agents that readily react with the halomethyl groups of the epihalohydrin polymer makes the composition less scorchy than the epihalohydrin polymer compositions of the prior art.

120 The vulcanizates prepared according to this invention find a wide utility especially where a high degree of resistance to deterioration in oils and fuel is required. Such requirements are found in various automotive and aircraft 130

hoses, fuel lines, mounts, grommets and gaskets.

The invention is further described by the following Examples.

5 EXAMPLE I.

- A series of blends were prepared using two crystalline alkadiene/acrylonitrile copolymers and two epichlorohydrin polymers. One epichlorohydrin polymer was a solid amorphous homopolymer having a chlorine content of 38% by weight and a Mooney viscosity (ML-4' @ 100°C) of 55 and identified hereinbelow as Hydrin*-1. The other epichlorohydrin polymer was a copolymer of epichlorohydrin and ethylene oxide containing 26% by weight chlorine and having a Mooney viscosity (ML-4' @ 100°C) of 100, and designated hereinbelow as Hydrin*-2.

*HYDRIN is a registered trademark.

- One crystalline alkadiene/acrylonitrile copolymer was an alternating copolymer of 50 mole % isoprene and 50 mole % of acrylonitrile (INAC) prepared in solution in methylene chloride using as the catalyst a preformed complex of ethyl aluminum dichloride and acrylonitrile mixed with vanadyl chloride. The copolymer showed an X-ray crystallinity of about 25% and an intrinsic viscosity of about 0.5 deciliter/gram measured at 30°C in dimethyl formamide. The second crystalline copolymer was made by copolymerizing in solution in methylene chloride a monomer mixture consisting of 35 parts isoprene, 15 parts butadiene-1,3 and 50 parts of acrylonitrile (BINAC). The catalyst was the same as used for INAC. The product was an alternating copolymer containing about 50 mole % of acrylonitrile, the units of which alternated with trans-1,4 units of isoprene and butadiene. It showed a crystallinity of about 20% measured by differential thermal method and an intrinsic viscosity of 0.7 dl/g measured at 30°C in dimethyl formamide.
- The crystalline copolymers were blended with epichlorohydrin polymers in proportions as shown in the table below and compounded using the following in parts by weight:

Polymer	100	
High Abrasion Furnace Black	40	
Zinc Oxide	3	50
Stearic Acid	0.5	
Benzothiazyl Disulfide	1.0	
Sulfur	1.5	
Alkylated Phenol Antioxidant	1.0	

The compounds were sheeted on a mill, then pressure molded and vulcanized in the mold at 145°C for 30 minutes. Two vulcanized sheets of each compound were reserved for testing stress-strain properties of unaged vulcanizates at room temperature and at 75°C. Other sheets were subjected to accelerated ageing for 72 hours in air at 100°C and 135°C, ASTM Fuel B at room temperature and ASTM #3 Oil at 100°C, respectively, before stress-strain testing.

The stress-strain and tear strength tests were carried out using an Instron Tester (Instron is a trade mark) on specimens cut out from the respective sheets. Hardness was determined according to ASTM-D-2280-68, low temperature stiffening (Gehman test) according to ASTM-D-1053-61, and tear strength. The results are presented in Table I. Table I also includes comparative data obtained for control vulcanizates made with unblended polymeric components. The epichlorohydrin homopolymer (Hydrin-1) was vulcanized using a different recipe since the sulfur system is not effective for vulcanizing such saturated polymers, as mentioned earlier. The recipe for Hydrin-1 containing Control I was as follows (wherein the amounts are parts by weight):

Hydrin-1	100	
HAF Carbon Black	40	85
Zinc Stearate	1	
Red Lead Oxide	5	
Mercaptoimidazoline	1.5	

The compound was sheeted, molded and vulcanized in the mold for 30 minutes at 145°C. The vulcanizate was tested for physical properties before and after ageing at conditions as listed above.

TABLE I

Compound No.	962 Control I*	959	960	198	190 Control II
<u>Polymer Composition (parts)</u>					
- Hydrin-1	100	50	—	50	—
- Hydrin-2	—	—	50	—	—
- BINAC	—	50	50	—	100
- INAC	—	—	—	50	—
Milling Behaviour	G**	E**	G	E	G
<u>Vulcanizate Properties</u>					
<u>Unaged Measured at 25°C/75°C</u>					
- Tensile Strength (kg/cm ²)	204/121	230/118	135/72	228/148	285/236
- Elongation (%)	420/260	460/380	250/230	470/380	390/470
- 100% Modulus (kg/cm ²)	38/46	45/31	60/34	50/35	50/33
- Tear Strength (kg/cm) (Trouser Test)	17/12	11/6	6/1	51***	47***
<u>Gehman Test</u>					
T-10/Fr.P. (°C)	-26/-34	-8/-15	-6/-18	—	0/-5
<u>Air Aged at 100°C/135°C</u>					
- Tensile Strength (kg/cm ²)	190/170	245/210	135/128	278/93	293/20
- Elongation (%)	310/230	320/70	150/20	360/70	300/10
- 100% Modulus (kg/cm ²)	45/60	75/—	95/—	75/—	77/—
- Tear Strength (kg/cm)	6/3	6/2.4	4/4	—	—
- Hardness (Shore A-2)	—	79/—	84/89	—	—
<u>Aged in #3 Oil at 100°C</u>					
- Tensile Strength (kg/cm ²)	178	195	115	155	275
- Elongation (%)	370	320	180	220	340
- 100% Modulus (kg/cm ²)	42	45	55	35	45
- Tear Strength (kg/cm)	5.2	8.6	3.4	—	—
- Hardness (Shore A-2)	62	53	71	—	—
- Volume Swell (%)	11.9	9.2	—	—	10.8
<u>Aged in Fuel B at 25°C</u>					
- Tensile Strength (kg/cm ²)	92	130	72	175	200
- Elongation (%)	250	300	160	300	310
- 100% Modulus (kg/cm ²)	30	32	40	50	35
- Tear Strength (kg/cm)	2.4	4.7	2.0	—	—
- Hardness (Shore A-2)	61	54	57	—	—
- Volume Swell (%)	12.0	22	—	11.6	24.2

* — Cured using red lead oxide and mercaptoimidazoline

** — G = Good; E = Excellent

*** — Graves Tear Test — ASTM-D-624 (data not directly comparable with the Trouser Test data)

The above results indicate that the vulcanized blend of Hydrin-1 and BINAC, Compound 959, was nearly as strong as Control II before and after ageing in oil and Fuel B.

It showed better low temperature properties, lower swell in #3 Oil and Fuel B and slightly better resistance to hot air ageing than BINAC. In comparison to Control I, Compound 959

was better in tensile strength, elongation, modulus before and after ageing in #3 Oil. Compounds 960 and 198 in which Hydrin-1 was replaced by Hydrin-2 and BINAC by INAC, respectively, showed in general similar results to those of Compound 959.

These results again indicate that Hydrin-1 and Hydrin-2 co-vulcanize with INAC and BINAC, respectively, in the sulfur vulcanization system and produce useful strong oil-resistant vulcanizates having a better balance of properties than the vulcanizates of the unblended polymeric constituents.

EXAMPLE II.

Hydrin-1 and BINAC of Example I were blended in different proportions as indicated in Table II, and compounded using the recipe of Example I. The compounds were sheeted, pressure molded and vulcanized for 30 minutes at 145°C. Two vulcanizate sheets were prepared of each compound; one sheet was aged for 72 hours in ASTM #3 Oil at 100°C, the other in ASTM Fuel B at room temperature.

Test specimens were cut from these sheets and used for testing stress-strain properties and hardness. The results are presented in Table II.

TABLE II

Compound No.	2	7	8
Hydrin-1/BINAC Weight Ratio	25/75	75/25	90/10
Aged 72 Hours in ASTM #3 Oil at 100°C			
- Tensile Strength (kg/cm ²)	241	105	37
- Elongation (%)	250	240	230
- 100% Modulus (kg/cm ²)	70	60	34
- Hardness (Shore A-2)	72	72	72
- Volume Swell (%)	6.3	6.8	6.3
Aged 72 Hours in ASTM Fuel B at Room Temperature			
- Tensile Strength (kg/cm ²)	178	81	31
- Elongation (%)	250	170	90
- 100% Modulus (kg/cm ²)	50	53	-
- Hardness (Shore A-2)	62	-	62
- Volume Swell (%)	16.2	13.5	13.1

The results indicate that the blends of Hydrin-1 and BINAC co-vulcanize in the presence of sulfur vulcanization system and produce oil-resistant vulcanizate. Even the 90/10 blend containing only 10% of the normally sulfur vulcanizable copolymer was satisfactorily vulcanized. The strength of vulcanized compositions aged in #3 Oil and Fuel B, respectively, decreased as the proportion of the crystalline nitrile copolymer was lowered from 75 to 10%; however, hardness and the degree of swell were not affected.

The 90/10 compound showed superior low temperature rubber properties and better resistance to hot air ageing in comparison to nitrile rubbers.

WHAT WE CLAIM IS:—

1. A sulfur vulcanizable elastomeric composition comprising a blend of an epihalo-

hydrin polymer and a crystalline alternating copolymer of (a) a conjugated alkadiene, component (a) containing not less than 40 mole % of a 2-alkyl alkadiene, and (b) an acrylic nitrile, said alternating copolymer being characterized by a crystallinity of 5—35%, as measured by X-ray diffraction in its unstretched state, and said composition being substantially free of agents capable of vulcanizing said epihalo-hydrin polymer.

2. The composition of claim 1 wherein said epihalo-hydrin polymer is a homopolymer of epichlorohydrin or a copolymer of 50—90 mole % epichlorohydrin and 10—50 mole % of an oxirane compound.

3. The composition of claim 2 wherein the oxirane compound is ethylene oxide.

4. The composition of any one of the preceding claims wherein said epihalo-hydrin polymer and said crystalline copolymer are

in a proportion from 90/10 to 10/90 in parts by weight.

5. The composition of any one of the preceding claims additionally containing 0.5—3 parts of sulfur and 0.5—4 parts of an accelerator selected from benzothiazyl disulfide, dialkyl dithiocarbamates and tetraalkyl thiuram disulfides, said parts being parts by weight per 100 parts by weight polymeric material.

6. The composition of any one of the preceding claims wherein said 2-alkyl alkadiene is a 2-alkyl butadiene-1,3.

7. The composition of claim 6 wherein said 2-alkyl butadiene-1,3 is isoprene.

8. The composition of claim 6 or claim 7 wherein said component (a) consists of 40—100 mole % isoprene and 0—60 mole % of butadiene-1,3.

9. A composition according to claim 1, and substantially as described with reference to the foregoing Example I or Example II.

10. A process of preparing a sulfur vulcanizate of an epihalohydrin polymer which comprises mixing said polymer with a crystalline alternating copolymer of (a) a conjugated alkadiene, component (a) containing not less than 40 mole % of a 2-alkyl alkadiene, and (b) an acrylic nitrile, said alternating copoly-

mer being characterized by a crystallinity of 5—35% as measured by X-ray diffraction in its unstretched state, and at least 0.5 parts by weight per 100 parts of the polymer mixture of sulfur to form a vulcanizable composition, and heating said vulcanizable composition in the absence of agents capable of vulcanizing said epihalohydrin polymer to produce a vulcanized rubber.

11. The process according to claim 10 wherein the vulcanizable composition additionally contains at least 0.5 parts, by weight per 100 parts by weight polymeric material, of an accelerator for sulfur vulcanization.

12. The process according to claim 10 or claim 11 wherein said 2-alkyl alkadiene is a 2-alkyl butadiene-1,3.

13. An oil-resistant vulcanized rubber prepared by the process as claimed in any one of claims 10 to 12.

14. A vulcanized rubber according to claim 13 and substantially as described with reference to the foregoing Example I or Example II.

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